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14. ABSTRACT

Molecular and radical chemisorption on ferroelectric oxides and on metals (Rh, Cu, Pt, Al, Pd, Ag) was studied with first-principles density functional theory (DFT). New methods were developed for computing the chemisorption energies of molecules to surfaces accurately within DFT. Oxide-supported metals were modeled as well, examining how oxide-metal bonding affects metal surface chemistry. Quantum Monte Carlo (QMC) calculations were performed on diatomic and polyatomic molecules, establishing the capability of computing atomic forces in molecules with QMC. Intermolecular interactions resulting from high molecular coverage were analyzed to understand saturation coverage. A direct dynamics approach was developed for computing the infrared emission signatures of combustion products, including vibrationally excited radicals and closed-shell molecules. The emission spectrum of vinyl radical C_2H_3 was computed and compared with recent experiments. It was demonstrated that molecular radicals stabilize ferroelectric polarization in $BaTiO_3$ nanowires and $PbTiO_3$ thin films. It was found

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Executive Summary—FA9550-04-1-0077 Final Report

Molecular and radical chemisorption on ferroelectric oxides and on metals
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computed and compared with recent experiments. It was demonstrated that
molecular radicals stabilize ferroelectric polarization in $BaTiO_3$ nanowires and
$PbTiO_3$ thin films. It was found that metal monolayers are significantly influenced
by ferroelectric oxide supports, opening the possibility of "switchable
nanocatalysts."

Student theses supported (all available through standard microfilm service):

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Dr. Valentino R. Cooper (Ph. D. Fall 2005)

http://repository.upenn.edu/dissertations/AAI3197662

Now a postdoc at Rutgers University physics (David Langreth/Karin Rabe)

Dr. Sara E. Mason (Ph. D. Spring 2007)

At http://repository.upenn.edu/dissertations soon.

Now an NRC postdoc at NIST physics (Anne Chaka)

Dr. Alexie M. Kolpak (Ph. D. Summer 2007)

At http://repository.upenn.edu/dissertations soon.

Now a MRSEC postdoc Yale chem/phys (John Tully/Sohrab Ismail-Beigi)

Mr. Myung Won Lee (Ph. D. expected 2008)

Ms. Elizabeth Sokol (B.A. spring 2007)

Now in medical school

Mr. Steven Young (B.A. spring 2006)

Honors:

Promotion to Professor of Chemistry, University of Pennsylvania (July 2006)

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Visiting professor of Chemistry, MIT (2005–2006)

Papers published during reporting period with Air Force support:

1. Eric J. Walter and Andrew M. Rappe, "Coadsorption of methyl radicals and oxygen on Rh (111)", *Surface Science* **549**, 265–72 (2004).

2. S. E. Mason, I. Grinberg, and A. M. Rappe, "First-principles extrapolation method for accurate CO adsorption energies on metal surfaces", *Phys. Rev. B Rapid Comm.* **69**, 161401 (1–4) (2004).

3. Y. Yourdshahyan, V. R. Cooper, A. M. Kolpak, and A. M. Rappe, "Catalytic behavior at the nanoscale: CO adsorption on Al_2O_3-supported Pt clusters", Proc. SPIE **5223**, 223–31 (2004).

4. S. B. Ziegeler, V. R. Cooper, and A. M. Rappe, "Visualization Value: Understanding Smart Materials From First Principles", NAVO MSRC Navigator, Naval Oceanographic Office Major Shared Resource Center, Fall issue 9–13 (2004). unrefereed.

5. M.-L. Bocquet, A. M. Rappe, and H.-L. Dai, "A density functional theory study of adsorbate-induced work function change and binding energy: Olefins on Ag(111)", *Molec. Phys.* **103**, 883–90 (2005).

6. M. W. Lee, M. Mella, and A. M. Rappe, "Electronic quantum Monte Carlo calculations of atomic forces, vibrations, and anharmonicities", *J. Chem. Phys.* **122**, 244103 (1–6) (2005).

7. V. R. Cooper, A. M. Kolpak, Y. Yourdshahyan, and A. M. Rappe, "Supported metal electronic structure: Implications for molecular adsorption", *Phys. Rev. B Rapid Comm.* **72**, 081409(R) (1–4) (2005). Selected for the *Virtual Journal of Nanoscale Science and Technology*, September 12, 2005 issue.

8. S. E. Mason, I. Grinberg, and A. M. Rappe, "Adsorbate-adsorbate interactions and chemisorption at different coverage studied by accurate ab initio calculations: CO on Transition Metal Surfaces", *J. Phys. Chem. B* **110**, 3816–22 (2006).

9. Fong, D.D.; Kolpak, A.M.; Eastman, J.A.; Streiffer, S.K.; Fuoss, P.H.; Stephenson, G.B.; Thompson, C.; Kim, D.M.; Choi, K.J.; Eom, C.B.; Grinberg, I., and A. M. Rappe, "Stabilization of Monodomain Polarization in Ultrathin $PbTiO_3$ Films", *Physical Review Letters*, **96**, 127601 1–4 (2006). Selected for the *Virtual Journal of Nanoscale Science and Technology*, April 10, 2006 issue.

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11. V. R. Cooper, A. M. Kolpak, Y. Yourdshahyan, and A. M. Rappe, "Oxide-supported metal thin-film catalysts: The how and why?" Nanocatalysts in technology Vol. 3, B. Zhou, ed. Springer-Verlag New York, 13–22 (2006).

12. M. W. Lee, M. Mella, and A. M. Rappe, "Electronic quantum Monte Carlo calculations of energies and atomic forces for diatomic and polyatomic molecules", Advances in Quantum Monte Carlo, J. B. Anderson and S. M. Rothstein, eds. ACS Symposium Series, No. 953, Oxford Univ Press, pp. 69–79 (2007).

13. A. M. Kolpak, I. Grinberg, and A. M. Rappe, "Polarization effects on the surface chemistry of $PbTiO_3$-supported Pt films" *Physical Review Letters* **98**, 166101 (1–4) (2007).

14. J. Li, U. G. Singh, J. W. Bennett, K. Page, J. Weaver, J.-P. Zhang, T. Proffen, A. M. Rappe, S. Scott, and R. Seshadri, "$BaCe_{1-x}Pd_xO_{3-\delta}$ ($0 \leq x \leq 0.1$): Redox controlled ingress and egress of palladium in a perovskite", *Chemistsry of Materials* **19**, 1418–26 (2007).

Introduction—FA9550-04-1-0077 Final Report

In the 2003–2006 grant period, we have pursued a program of research in highly accurate calculations of small molecules important for combustion chemistry as well as in the interactions at the gas-surface interface important in heterogeneous catalysis. The scientific research was accompanied and enabled by methodological developments necessary to carry out the research program. Computational Quantum Monte Carlo (QMC) and density functional theory (DFT) methods were used to reveal the behavior of chemically complex systems, to develop fundamental models, and to explore novel systems.

Our objective was to attain understanding of chemical interactions in combustion and catalysis at realistic conditions. This requires one to go beyond simple model chemisorption systems (for heterogeneous catalysis) and to achieve an improved accuracy of calculations (for combustion).

Combustion

In the studies of small molecules we have further developed our QMC methodology, computing vibrational frequencies and anharmonicities for the first time. We have also extended our QMC effort to polyatomic molecules, studying benzene as an example.

To develop the methodology for computing small molecule properties at high temperatures, we developed a direct dynamics approach for computing the infrared emission signatures of combustion products, including vibrationally excited radicals and closed-shell molecules. The emission spectrum of vinyl radical $\cdot C_2H_3$ was computed and compared with recent experiments.

Heterogeneous catalysis

Heterogeneous catalysis is crucial for many industrial processes, including combustion, rocket propulsion and pollution control. Catalysis is a complex process that takes place at high temperature and pressure, involving multiple reactions between a variety of adsorbates. For many Air Force applications, the most promising catalysts are the reactive surfaces of metal clusters supported by oxides. Theoretical and experimental research has largely elucidated the interactions of simple metal surfaces with simple molecular adsorbates. However, for practical integration of rational design principles into the development of better catalysts, chemistry on the complex catalyst surface under realistic reaction conditions must be studied. There are three main differences between the simple models of adsorption typically studied and the real heterogeneous catalysis: 1) the variations in metal surface geometry, 2) the presence of high coverage of adsorbates, often with more than one chemical species, and 3) the impact of oxides either as support materials for the metal surface or due to their direct participation in catalysis. Our research during the grant period was focused on exploring these three aspects of realistic catalytic systems.

1) The impact of changes in metal surface geometry

To study the influence of surface geometry on reactivity, we performed calculations for molecular and atomic adsorption on the (111) and (100) surfaces of Rh, Pt and Pd in a variety of strain states. The large number of surfaces studied allowed us to determine the magnitude of the effects of changes in surface geometry on surface reactivity. This set of systems was also used to develop a new procedure for more accurate computation of chemisorption energies, enabling the studies of adsorbate-adsorbate interactions described below.

2) Adsorbate-adsorbate interactions at high coverage.

To elucidate the impact of adsorbate-adsorbate interactions, which are present at high pressures and atomic coverages in typical heterogeneous catalysis, we have examined coadsorption of methyl radicals and oxygen on the Rh (111) surface and the interactions of adsorbed CO molecules on a variety of metal surfaces. The large number of metal surfaces and the simplicity of the CO adsorbate allowed us to elucidate the impact of surface geometry and reactivity on the inter-adsorbate interactions. On the other hand, the in-depth study of CO+O/Rh (111) system, showed how the geometry and energetics of the more complex adsorbates such as $\cdot CH_3$ are affected by increased concentration of O atoms, which are chemically very different from the $\cdot CH_3$ adsorbates.

3) The effect of the oxide support.

We have investigated the impact of the oxide support on the reactive properties of the metal surfaces. We began our studies with examination of CO adsorption on alumina-supported platinum surface. CO adsorption has now been well understood on simple metal surfaces; this makes it easy to isolate the role of the oxide support and the impact it has on the metal surface chemistry. Building on the results of this study, which showed that surface dipole is crucial in determining the reactivity of the oxide-supported metals, we have studied atomic and molecular adsorption on Pt metal supported by the $PbTiO_3$ complex oxide. The polarization of this oxide can be reversibly switched, which allows precise

control of chemistry of the metal. This makes such systems "switchable catalysts", meaning that their catalytic properties can be dynamically changes by switching of the oxide polarization. In addition to changing the chemistry of the metal surface, oxide supports can also protect the metal nanoparticles from sintering and oxidation, two processes that degrade catalytic performance. To study this kind of metal/oxide interactions, we have also investigated the reversible formation of Pd nanoparticles on the $BaCeO_3$ driven by changes in thermodynamic conditions. Finally, to investigate the direct participation of oxides in catalytic processes, we have studied atomic and molecular adsorption on the surfaces of $PbTiO_3$ and $BaTiO_3$ oxides.

Computational Approach—FA9550-04-1-0077 Final Report: Description of equipment, set up, and procedures, description of computational codes (collected/computed data reported in published papers) (Computational code URLs provided below)

Density functional theory (DFT) has repeatedly proved itself as a powerful, efficient, and accurate tool for analyzing and predicting phenomena in metallic, semiconducting, and insulating systems. Density functional theory relies on a reformulation of the quantum mechanical problem, and is able to compute the ground state total energy of a system without finding the many-body wavefunction, if the ground state charge density is known. The exact functional needed to obtain the total energy from the charge density is unknown. However several excellent first-principles approximations to the functional exist, such as the generalized gradient approximation (GGA). These approximations have been well tested and are highly successful for computing the properties of real materials. We utilize the DFT formulation within an efficient approach, which scales approximately as N^2. This favorable scaling makes accurate descriptions of large systems possible. We opt to represent the Kohn-Sham orbitals in a plane wave basis set. This basis set is rigorously complete, treats wavefunctions that differ in direct-space localization (i.e. atom-centered, bond-centered, diffuse, etc.) in an equal, unbiased manner and allows one to take advantage of fast

Fourier transform algorithms, significantly increasing the efficiency of calculations. The plane wave basis set is also a natural choice for studies of extended systems with periodic boundary conditions. Perhaps the main disadvantage of the plane-wave basis set is that many basis functions are required to accurately describe highly localized orbitals, such as the orbitals of core electrons. In order to retain the efficiency of the plane-wave approach, the core electrons are combined with the nuclei into a weaker effective potential, or a pseudopotential, which is the potential felt by the valence electrons during the calculation. Treating the core electrons in this fashion only introduces a small amount of error into the calculation since the core electrons do not participate in bonding to any significant extent within the system. However, the construction of an appropriate pseudopotential must be done with great care in order to insure the natural physical and chemical properties of the system are maintained.

Our group has been at the forefront of research on high-quality pseudopotentials, elucidating quantitative atomic criteria for pseudopotential accuracy in transition metal, oxide and molecular systems. We also currently maintain a pseudopotential generation package OPIUM that provides for easy and flexible generation of pseudopotentials for many different standard DFT codes. OPIUM is available at http://opium.sourceforge.net. This computational method, including pseudopotentials, plane waves, and approximations to density functional theory, has been applied successfully to a wide variety of systems including insulators, semiconductors, metals, surfaces, interfaces, clusters, and molecules.

To perform ionic relaxations we used a quasi-Newton local minimization method. Due to our use of periodic boundary conditions, the effects of applied stress and strain on adsorption energetics and reaction pathways can be easily modeled by carrying out calculations at the appropriate supercell lattice constants.

To improve accuracy of DFT-GGA calculations of chemisorption, we have designed a first-principles extrapolation procedure that agreed with experimentally determined preferred adsorption sites for the eight substrates we

studied. Our method greatly reduces DFT-GGA over-binding of chemisorption energies in these systems. This new technique makes us ideally suited to explore chemisorption and catalysis on novel surfaces and we expect to extend to molecules other than CO in the near future.

Several methods were used to correlate changes in observables such as chemisorption energies and reaction barriers with changes in oxide and metal chemical bonding. Analysis of local atom projected density of states has been used extensively to link electronic structure of the metal surface to chemisorption energy, elucidating the role of different transition metal d-orbitals in the chemisorption bond. We also used induced charge density plots to examine charge transfer and rearrangement effects particularly important for the somewhat ionic and polar oxide systems studied in this proposal. Changes in adsorbate bonding are investigated through the computation of vibrational frequency shifts; this also allows for direct comparison with experimental data.

We have used two pseudopotential plane wave codes in order to carry out proposed research. We have programmed our own code that is on par with the state of the art commercial codes in terms of accuracy and efficiency. This code has been written from scratch by the group and is optimized for performance on Linux Beowulf, CRAY X1 and SGI O3000 platforms. It is advantageous to have complete knowledge of the code and we frequently upgrade the efficiency and accuracy of our program. Our code uses the designed non-local optimized pseudopotentials, employing methodology created by the principal investigator and his students. We also use the abinit and DACAPO codes (http://www.abinit.org/ and http://dcwww.camd.dtu.dk/campos/Dacapo/intro.html) both of which are freely available online. These codes allows one to use ultra-soft or PAW pseudopotentials, which are more efficient for some systems. We have extensive experience with all codes, and we also use the two programs to double-check our calculations, making sure that surprising results are genuine.

Results—FA9550-04-1-0077 Final Report: Comprehensive technical summary of the significant work accomplished

Combustion

In our development of highly accurate quantum Monte Carlo methods, we have calculated atomic forces for first-row monohydrides and carbon monoxide within electronic quantum Monte Carlo (QMC). Accurate and efficient forces are achieved by using an improved method for moving variational parameters in variational QMC. Newton's method with singular value decomposition (SVD) is combined with steepest-descent (SD) updates along directions rejected by the SVD, after initial SD steps. Dissociation energies in variational and diffusion QMC agree well with the experiment. The atomic forces agree quantitatively with potential-energy surfaces, demonstrating the accuracy of this force procedure. The harmonic vibrational frequencies and anharmonicity constants, derived from the QMC energies and atomic forces, also agree well with the experimental values. This work was then extended to QMC studies of structure and vibrations of benzene. (M. W. Lee, M. Mella, and A. M. Rappe, *J. Chem. Phys.* **122**, 244103 (1–6) (2005)).

We have also used *ab initio* methods to study structure and spectroscopy of transient radicals important in atmospheric systems and combustion reactions. We used direct molecular dynamics and electronic structure calculations using DFT within the GAMESS package to understand vibrationally hot but electronically cold radical dynamics. These were used to characterize the complex interaction of rotation, alpha-proton motion, and anharmonic effects, and their influence on the IR spectrum. The results of this study are now being prepared for submission to *Journal of Chemical Physics*.

Heterogeneous Catalysis.

1) The impact of changes in metal surface geometry

To enable accurate computation of adsorption energetics, we have addressed the previous inability of DFT method to predict the correct adsorption

site and energy for the model CO/metal adsorption systems. We showed that a simple first-principles correction based on the difference between the singlet-triplet CO excitation energy values obtained by DFT and high-level quantum chemistry methods yield accurate CO adsorption properties on a variety of metal surfaces. We demonstrated a linear relationship between the CO adsorption energy and the CO singlet-triplet splitting (ΔE_{S-T}). Converged DFT calculations underestimate the CO ΔE_{S-T}, whereas coupled-cluster and configuration-interaction (CI) calculations reproduce the experimental ΔE_{S-T}. The dependence of E_{chem} on ΔE_{S-T} was used to extrapolate E_{chem} for the top, bridge, and hollow sites for the (100) and (111) surfaces of Pt, Rh, Pd, and Cu to the values that correspond to the coupled cluster and CI ΔE_{S-T} value. The correction reproduces experimental adsorption site preference for all cases and obtains E_{chem} in excellent agreement with experimental results. (S. E. Mason, I. Grinberg, and A. M. Rappe, *Phys. Rev. B Rapid Comm.* **69**, 161401 (1–4) (2004)).

In our study of the interplay between metal surface chemistry and metal surface geometry changes due to facet and strain, we have demonstrated that variations in molecular chemisorption energy on different metals, different surface terminations, and different strain conditions can be accounted for by orbital-specific changes in the substrate electronic structure. We applied this analysis to a density functional theory data set, spanning three metals, two surface terminations, and five strain states. A crucial aspect of our analysis is decomposition of the *d*-band into contributions from the five *d* atomic orbitals. This provides a representation of the energy levels of the substrate that are directly relevant to the chemisorption bond, leading to strong correlation with chemisorption trends. This study is currently under review at *Journal of Physical Chemistry C*.

We have also used DFT calculations to study the dependence of the dissociative (associative) chemisorption energies of CO, N_2, NO, and O_2 (C, N, O) on (111) surfaces of Pt, Rh, Pd, and Cu at different in-plane strains. Observed trends in the strain dependence of chemisorption energies are linked to metal electronic properties. We then used the results in kinetic modeling of

volcano curves to highlight the shift in optimal modeled catalyst activity induced by strain for given reaction conditions (temperature, pressure). The results of this study are currently being prepared for submission to *Surface Science*.

2) Adsorbate-Adsorbate interactions:

We use density functional theory (DFT) with the generalized gradient approximation (GGA) and our first principles extrapolation method for accurate chemisorption energies (see above) to calculate the chemisorption energy for CO on a variety of transition metal surfaces for various adsorbate densities and patterns. We identify adsorbate through-space repulsion, bonding competition, and substrate-mediated electron delocalization as key factors determining the preferred chemisorption patterns for different metal surfaces and adsorbate coverages. We discuss how the balance of these interactions, along with the inherent adsorption site preference on each metal surface, can explain the observed CO adsorbate patterns at different coverages. (S. E. Mason, I. Grinberg, and A. M. Rappe, *J. Phys. Chem. B* **110**, 3816–22 (2006)).

The co-adsorption of CH_3 and O on Rh(111) is another excellent example of the importance of substrate-mediated interadsorbate interactions. Our DFT results show strong adsorption at all high-symmetry sites with methyl in two possible orientations. We find strong evidence for a multi-center bond between methyl and the surface rhodium atoms. Such multi-center bonding leads to C–H bond depletion and is the cause of experimentally observed mode-softening for methyl on Rh(111). Our results for CH_3 and O coadsorption system suggest a new model for the effect of O on CH_3. Analysis of charge density differences shows that the dominant initial effects of O coadsorption are the removal of charge from the C-surface bond and the transfer of charge to the C–H bond, which leads to the disappearance of mode-softening, in agreement with experimental observations. (E. J. Walter and A. M. Rappe, *Surface Science* **549**, 265–72 (2004)).

3) Impact of oxide support

In our initial study of the role of oxide support in catalysis, we examined the electronic structure of substrate-supported metal films with *ab initio* methods. We predict a coexistence between charge-transfer valence-bond states and bandlike metallic states. The role of the support composition in determining the balance of bond and band states is elucidated for Pt on Al- and O-terminated α-Al_2O_3, and we revealed how this coexistence evolves with metal film thickness. Using CO chemisorption as a probe of metal film electronic structure, we demonstrated that this combination of bond and band effects leads to significant changes in surface chemistry. In, particular we found that the surface dipole created by the interaction at the metal-oxide interface played a crucial role in determining the chemistry of the gas-metal thin film interface. (V. R. Cooper, A. M. Kolpak, Y. Yourdshahyan, and A. M. Rappe, *Phys. Rev. B Rapid Comm.* **72**, 081409(R) (1–4) (2005)).

Our realization of the importance of the surface dipole for reactivity leads us to suggest a new paradigm of dynamical control of surface structure and reactivity by supporting the catalytic metal on an oxide with a switchable polarization. To demonstrate this paradigm, we performed density functional theory calculations of the adsorption of several molecules and atoms to the surface of ultrathin Pt (100) films supported on ferroelectric $PbTiO_3$. We show that reorienting the polarization direction of the substrate can dramatically change the chemisorption energies of CO, O, C, and N and alter the reaction pathways for dissociation of CO, O_2, N_2, and NO. We elucidated the structural and electronic effects of a polarized substrate on the metal surface suggested potential applications in tunable catalysis. (A. M. Kolpak, I. Grinberg, and A. M. Rappe, *Physical Review Letters* **98**, 166101 (1–4) (2007)).

Dynamical changes in stoichiometry of the surface in the metal/oxide system can also be used to improve catalytic performance by reversibly generating metal nanoparticle on the oxide surface. In collaboration with experimental groups at UC-Santa Barbara, we have demonstrated that Pd^{2+} ions can be substituted for Ce in perovskite $BaCeO_3$ and that, under oxidizing conditions, $BaCe_{1-x}Pd_xO_{3-x}$

($0<x<0.1$) compositions can be prepared. The structure of the host compound and models for Pd substitution have been studied using density functional theory, which has provided a detailed *local* description of the structure. The Pd^{2+}-containing perovskite phases extrude elemental face-centered cubic palladium nanoparticles when heated in a reducing atmosphere. This elemental palladium is re-absorbed as ions into the perovskite lattice upon heating in flowing oxygen. Such *cyclable* ingress and egress of palladium protects the catalytically active palladium nanoparticles from oxidation and sintering that usually take place under oxidizing conditions. (J. Li, U. G. Singh, J. W. Bennett, K. Page, J. Weaver, J.-P. Zhang, T. Proffen, A. M. Rappe, S. Scott, and R. Seshadri, *Chem. Mater.* **19**, 1418–26 (2007)).

Finally, to examine the direct interactions between the gas phase and the oxide surface, we have studied chemisorption on $PbTiO_3$ and $BaTiO_3$ surfaces. We find that chemisorption of OH radicals is strongly favored under ambient conditions. Interestingly, we also find that the adsorbates can induce a phase transition in the oxide film, stabilizing polarization not only on the surface but also throughout the bulk of the oxide. (D. D. Fong *et al.*, *Physical Review Letters*, **96**, 127601 1–4 (2006) and J. E. Spanier *et al.*, *Nano Letters* **6**, 735–9 (2006)).

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